

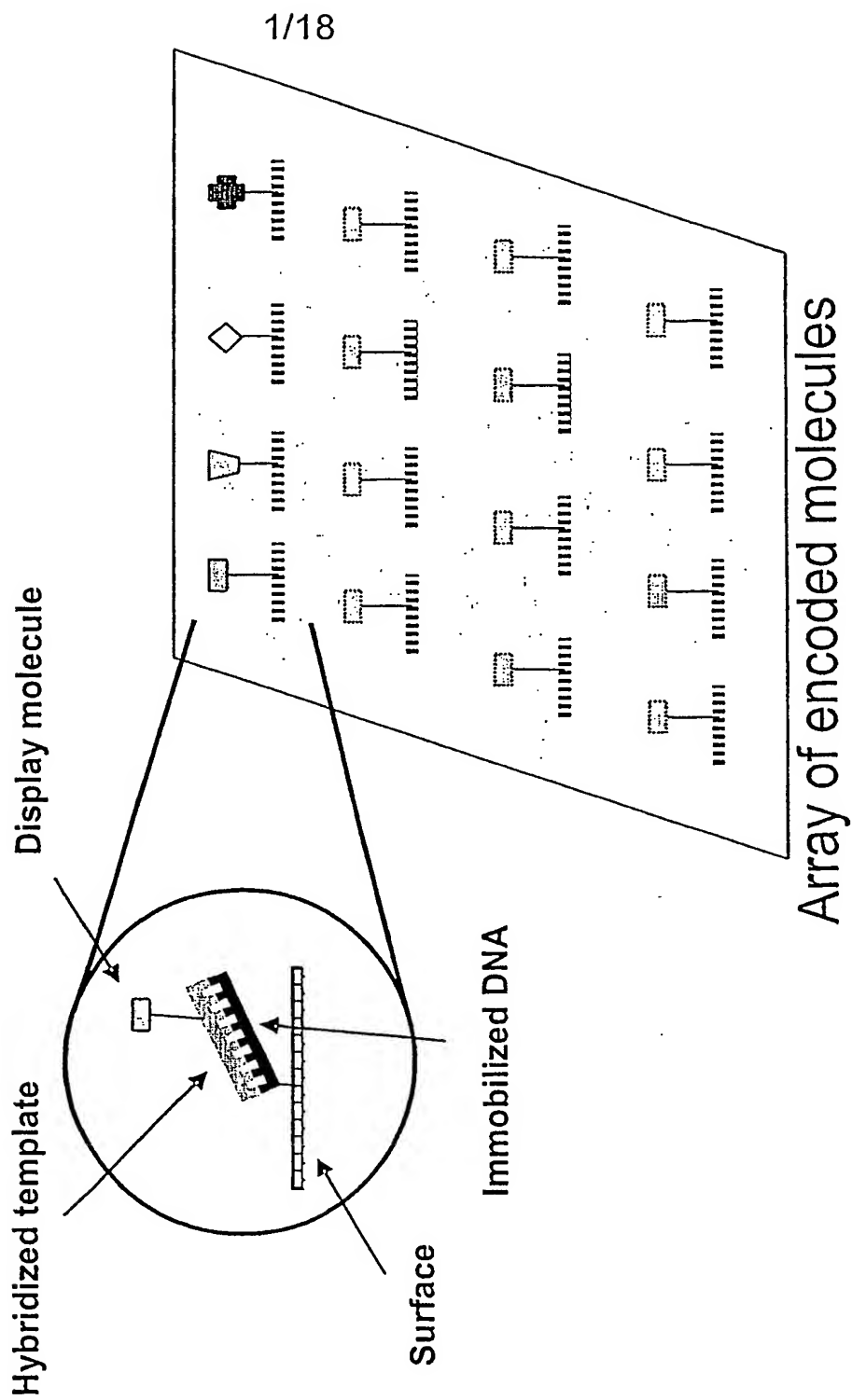
Fig. 1

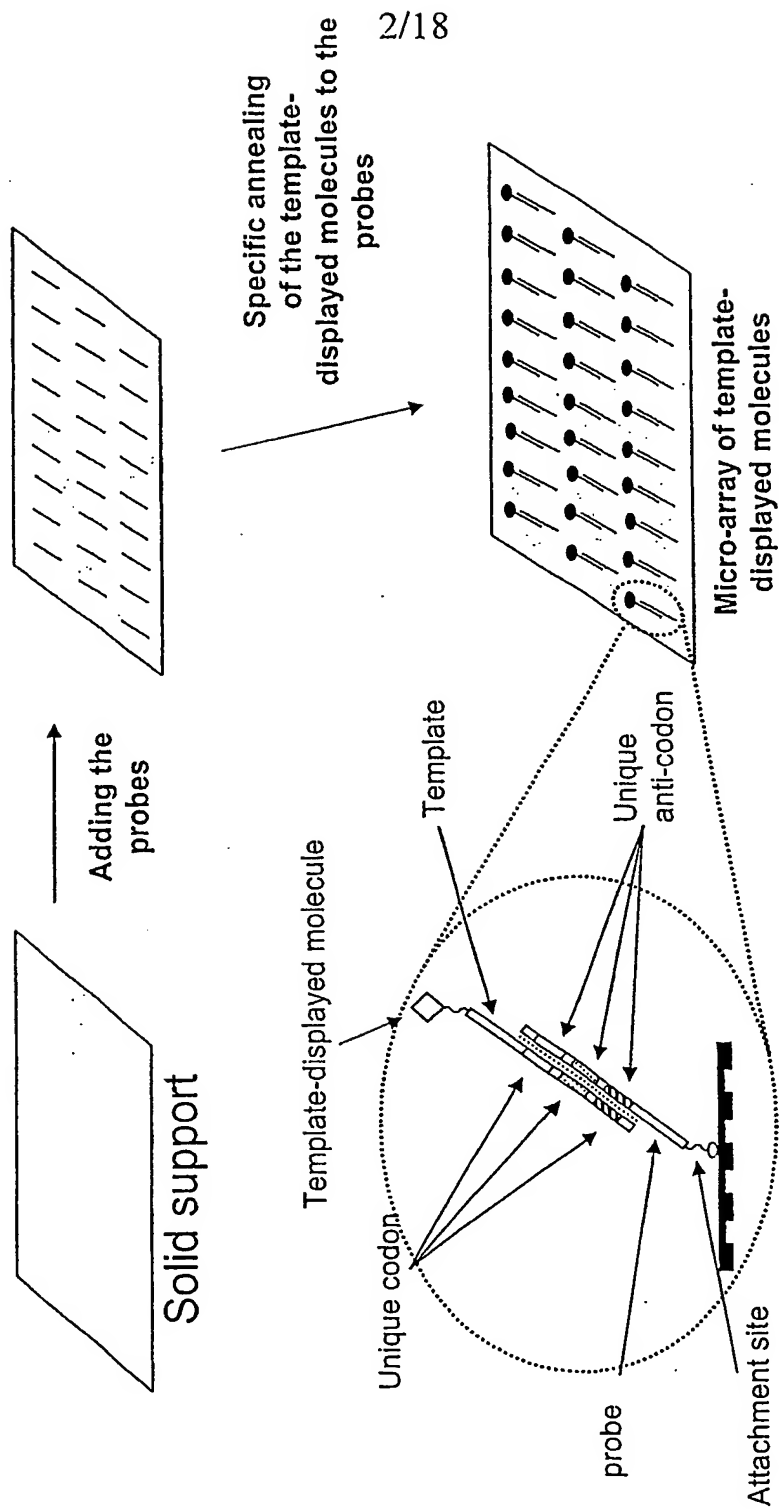
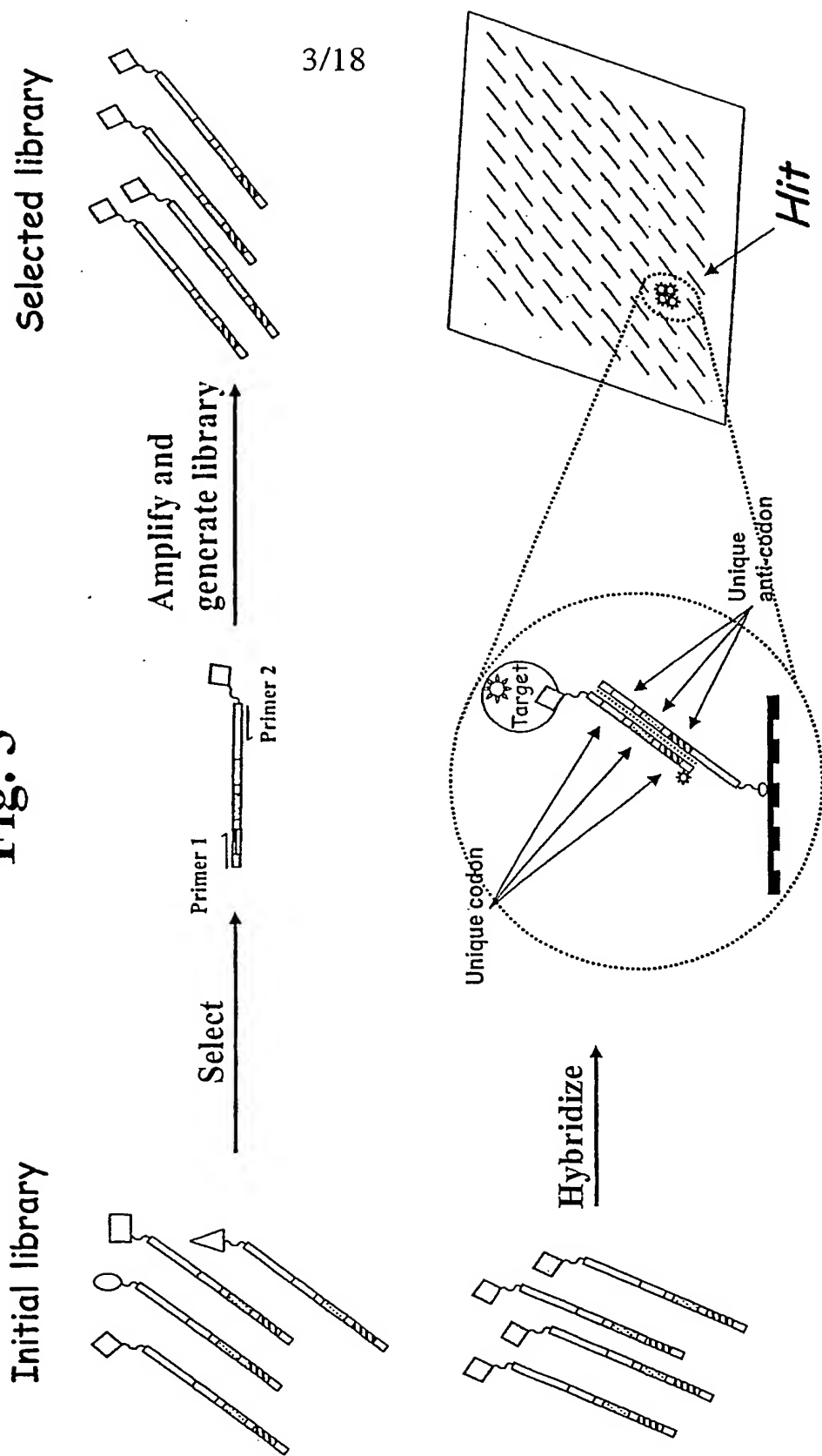
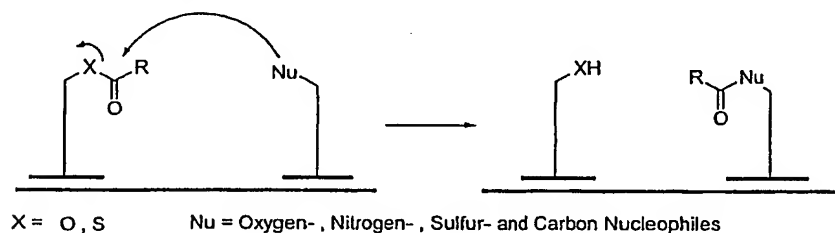
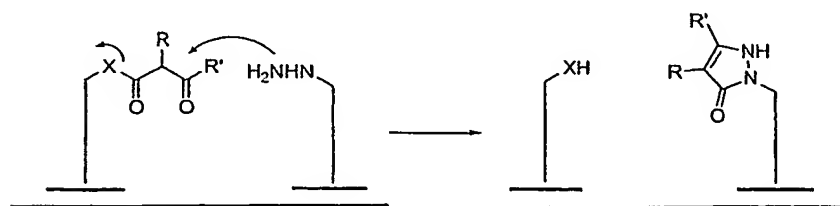
Fig. 2

Fig. 3



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Fig. 4**A. Acylating monomer building blocks - principle****B. Acylation****Amide formation by reaction of amines with activated esters****C. Acylation****Pyrazolone formation by reaction of hydrazines with β -Ketoesters**

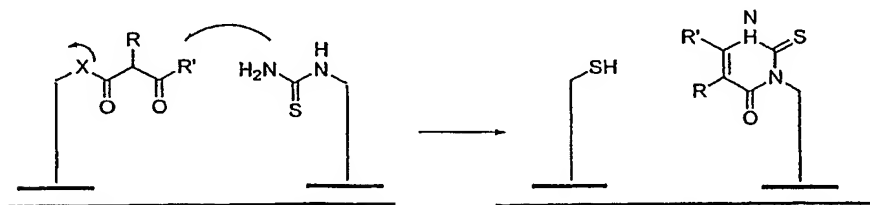
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D. Acylation

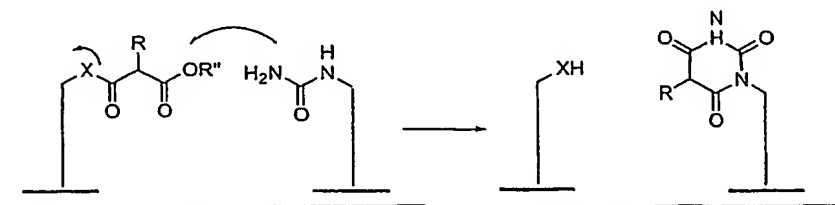
Isoxazolone formation by reaction of hydroxylamines with β -Ketoesters

**E. Acylation**

Pyrimidine formation by reaction of thioureas with β -Ketoesters

**F. Acylation**

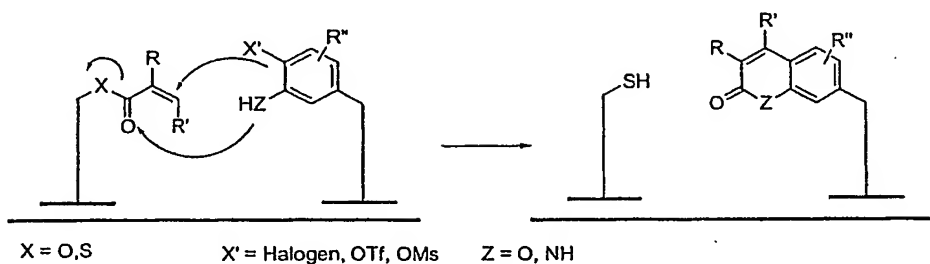
Pyrimidine formation by reaction of ureas with Malonates



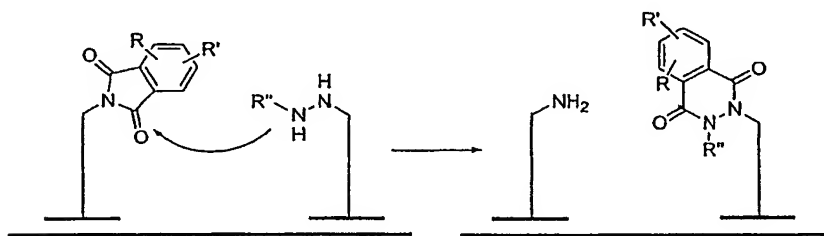
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G. Acylation

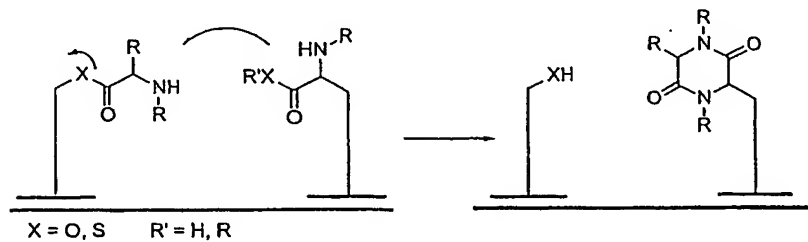
Coumarine or quinolinon formation by a Heck reaction followed by a nucleophilic substitution

**H. Acylation**

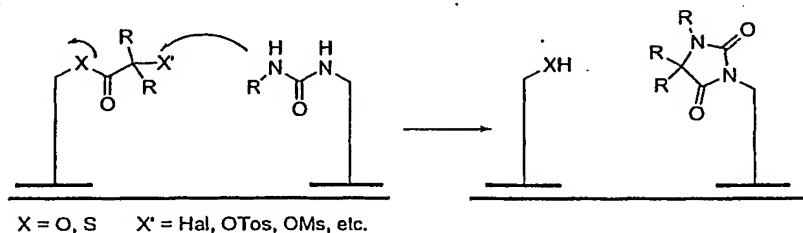
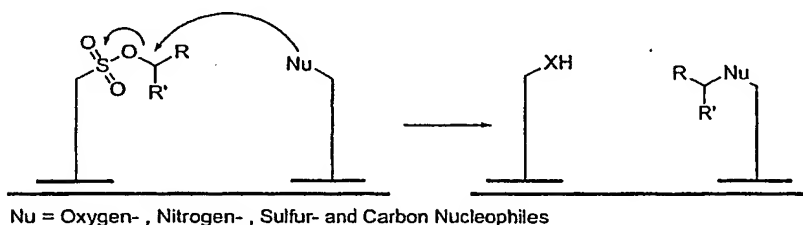
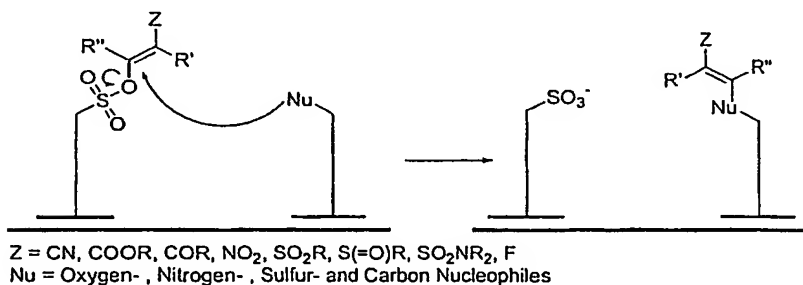
Phthalhydrazide formation by reaction of Hydrazines and Phthalimides

**I. Acylation**

Diketopiperazine formation by reaction of Amino Acid Esters



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J. Acylation**Hydantoin formation by reaction of Urea and α -substituted Esters****K. Alkylating monomer building blocks - principle****Alkylated compounds by reaction of Sulfonates with Nucleophiles****L. Vinylating monomer building blocks - principle**

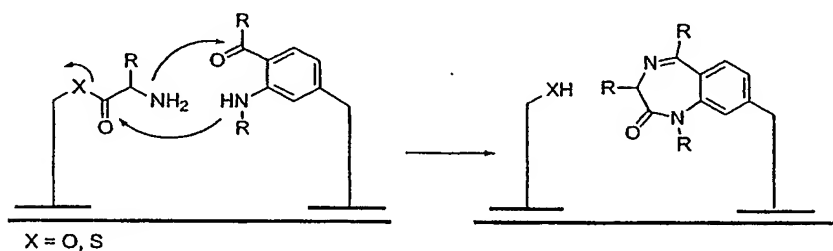
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M. Heteroatom electrophiles

Disulfide formation by reaction of Pyridyl disulfide with Mercaptanes

**N. Acylation**

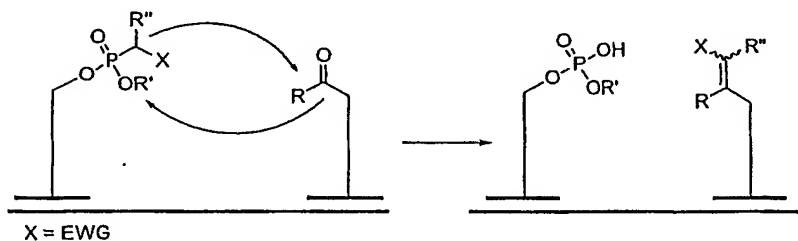
Benzodiazepinone formation by reaction of Amino Acid Esters and Amino Ketones



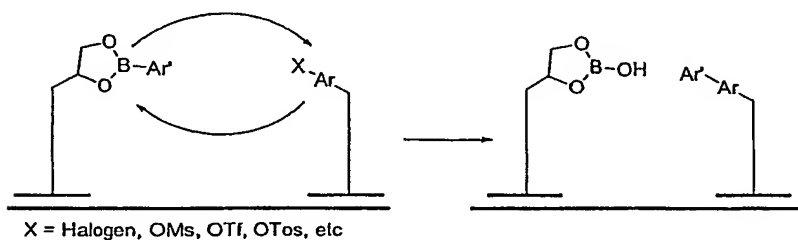
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O. Wittig/Horner-Wittig-Emmons reagents

Substituted alkene formation by reaction of Phosphonates with Aldehydes or Ketones

**P. Arylation**

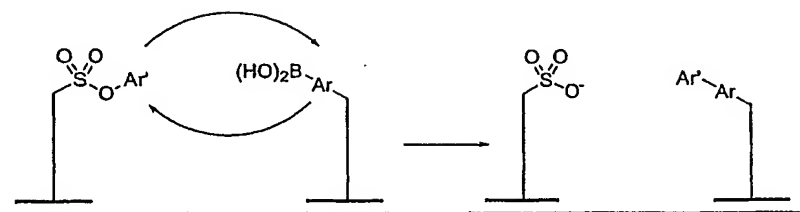
Biaryl formation by the reaction of Boronates with Aryls or Heteroaryls



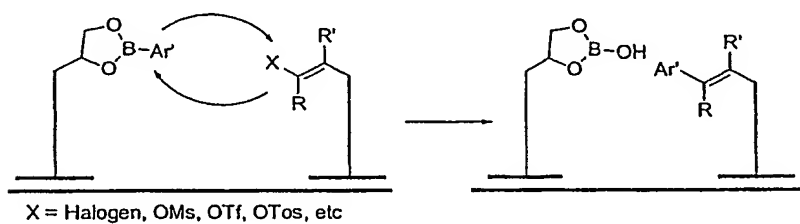
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Q. Arylation

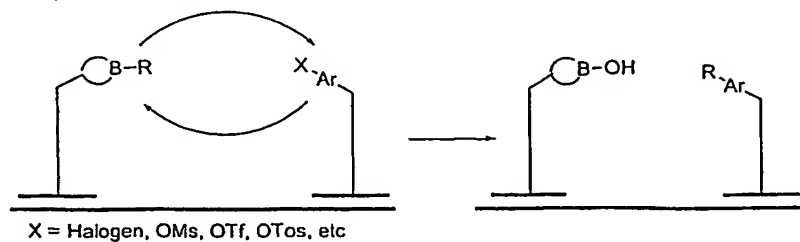
Biaryl formation by the reaction of Boronates with Aryls or Heteroaryls

**R. Arylation**

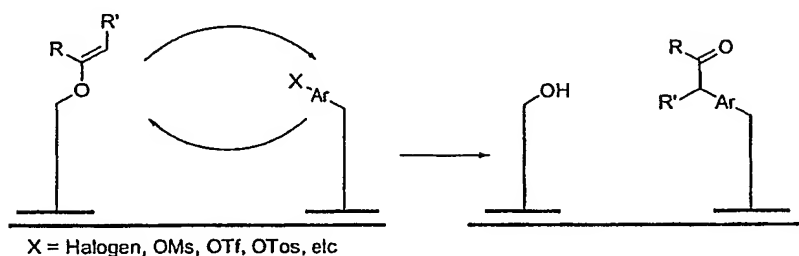
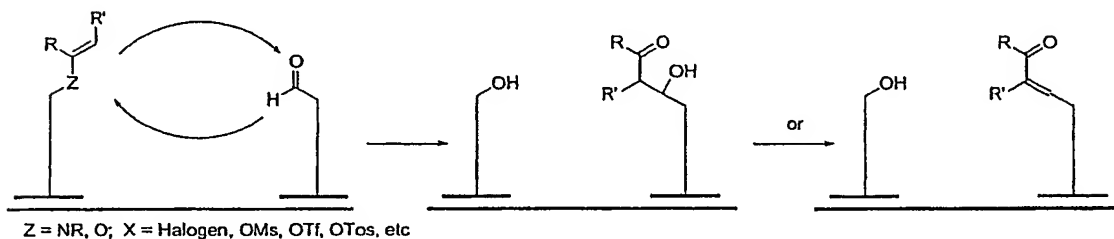
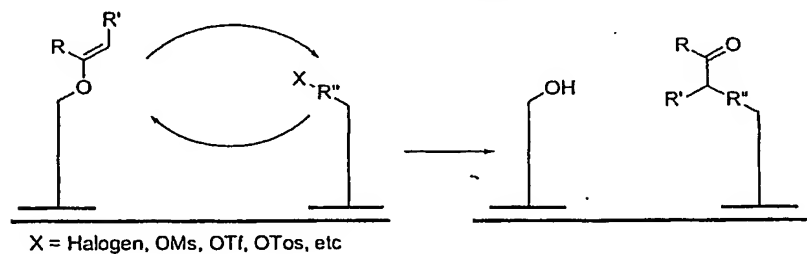
Vinylarene formation by the reaction of alkenes with Aryls or Heteroaryls

**S. Alkylation**

Alkylation of arenes/hetarens by the reaction with Alkyl boronates

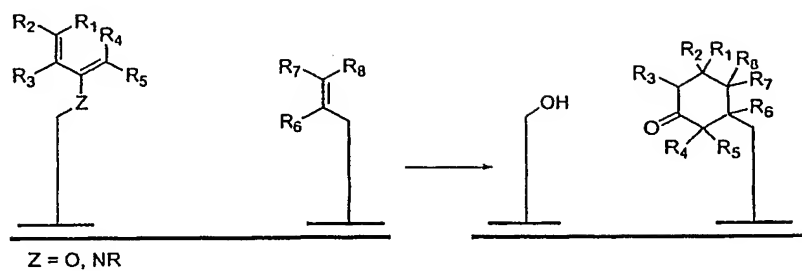


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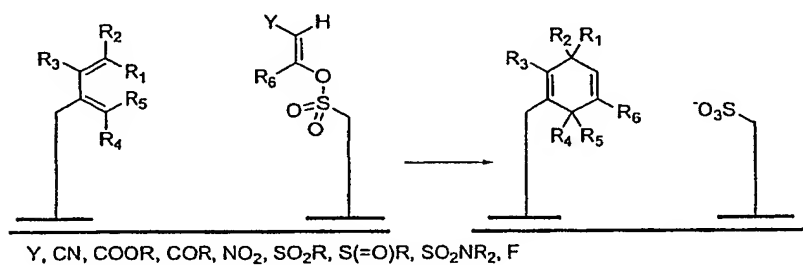
T. Alkylation**Alkylation of arenas/hetarenes by reaction with enoethers****U. Condensations****Alkylation of aldehydes with enoethers or enamines****V. Alkylation****Alkylation of aliphatic halides or tosylates with enoethers or enamines**

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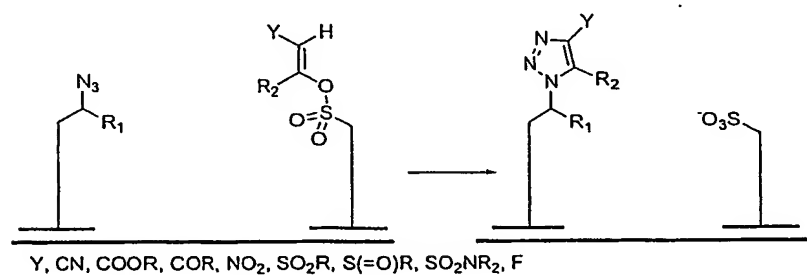
W. [2+4] Cycloadditions



X. [2+4] Cycloadditions



Y. [3+2] Cycloadditions



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Z. [3+2] Cycloadditions

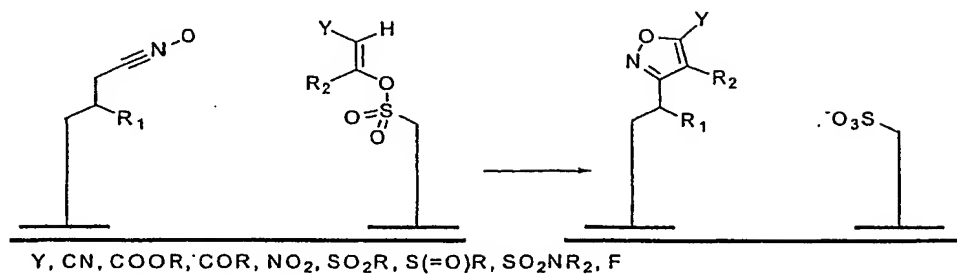
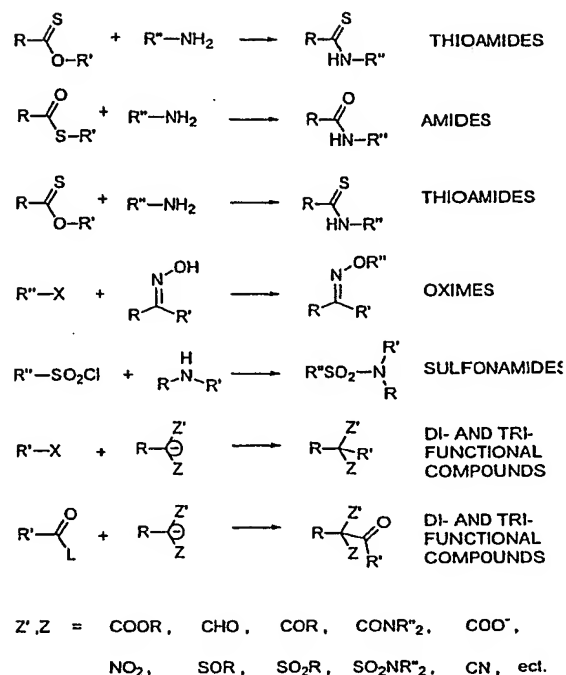
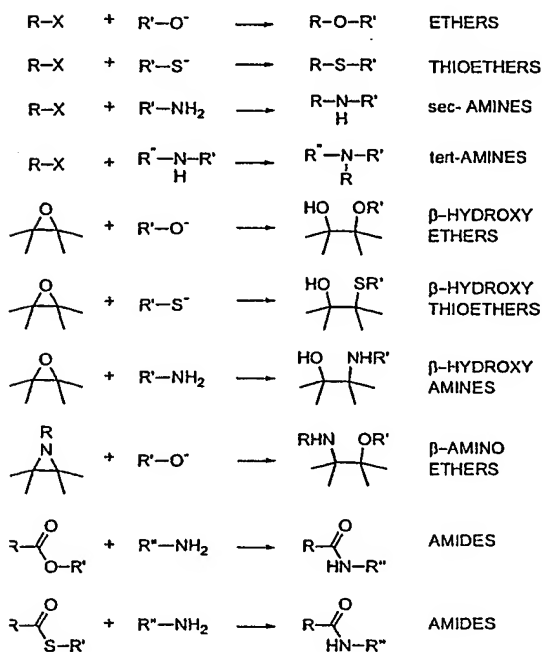


Fig. 5

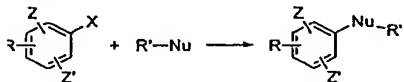
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Nucleophilic substitution reaction



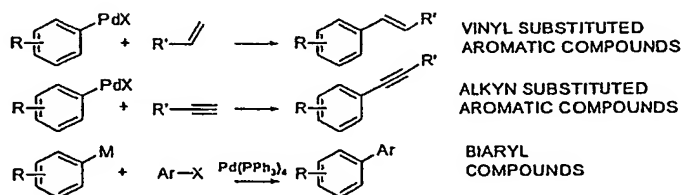
Aromatic nucleophilic substitution

SUBSTITUTED AROMATIC COMPOUNDS



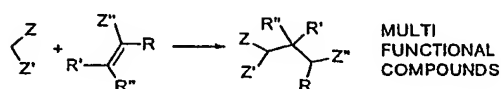
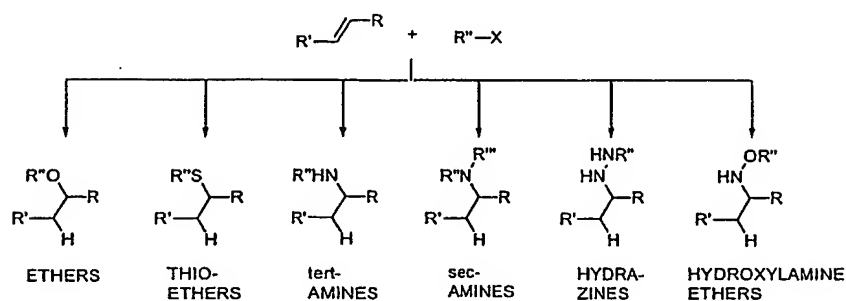
Nu = Oxygen-, Nitrogen-, Sulfur- and Carbon Nucleophiles
 X = F, Cl, Br, I, OSO₂CH₃, OSO₂CF₃, OSO₂TOL, . . . etc.
 Z', Z = COOR, CHO, COR, CONR₂⁺, COO⁻, CN,
 NO₂, SOR, SO₂R, SO₂NR₂⁺, . . . ect.

Transition metal catalysed reactions

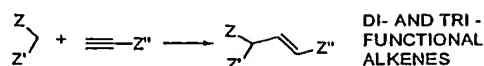


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Addition to carbon-carbon multiple bonds

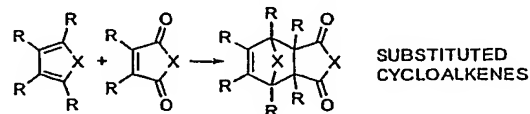
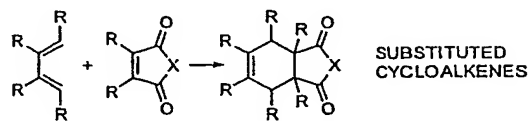
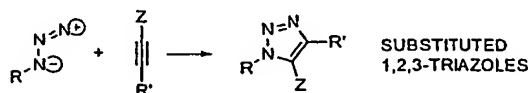
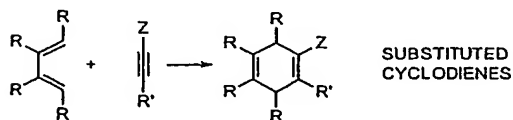
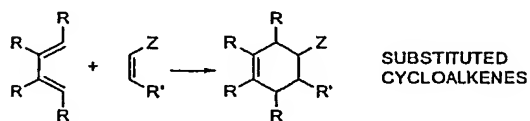


$\text{Z} = \text{H, Alkyl, Z', Ar}$
 $\text{Z}'' = \text{COOR, CHO, COR, CONR}_2, \text{CN, NO}_2, \text{SOR, SO}_2\text{R, SO}_2\text{NR}_2, \text{ etc.}$
 $\text{Z}' = \text{Z}'' \quad \text{R} = \text{R}', = \text{R}'', = \text{Z}$



$\text{Z} = \text{H, Alkyl, Ar,}$
 $\text{Z}'' = \text{Z', Alkyl, Ar,}$
 $\text{Z}' = \text{COOR, CHO, COR, CONR}_2, \text{CN, NO}_2, \text{SOR, SO}_2\text{R, SO}_2\text{NR}_2, \text{ etc.}$

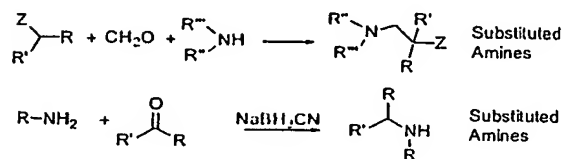
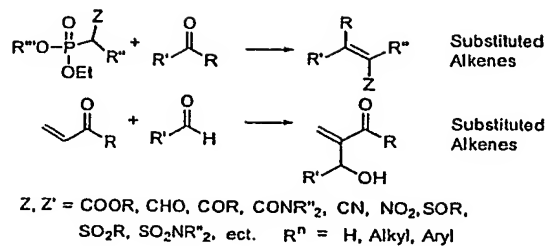
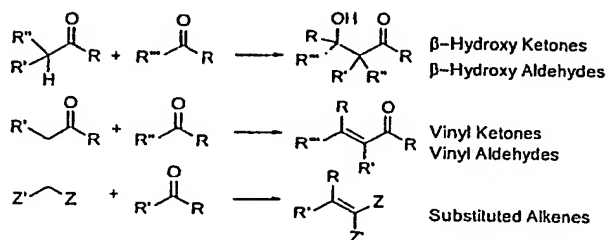
Cycloaddition to multiple bonds



$\text{Z} = \text{COOR, CHO, COR, COOH, COAr, CN, NO}_2, \text{Ar, CH}_2\text{OH, CH}_2\text{NH}_2, \text{CH}_2\text{CN, SOR, SO}_2\text{R etc.}$
 $\text{R} = \text{H, Alkyl, Ar, Z} \quad \text{X} = \text{O, NR, CR}_2, \text{S,}$

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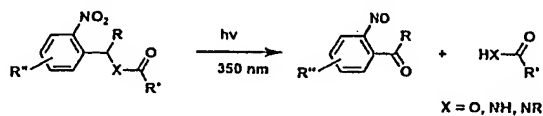
Addition to carbon-hetero multiple bonds


 $\text{Z} = \text{COOR}, \text{CHO}, \text{COR}, \text{SOR}, \text{SO}_2\text{R}, \text{CN}, \text{NO}_2, \text{ect.}$
 $\text{R} = \text{R}', \text{H}, \text{Alkyl}, \text{Ar},$
 $\text{R}'' = \text{R}''', \text{H}, \text{Alkyl}, \text{COR},$

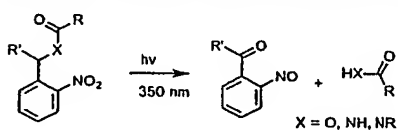
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Fig. 6

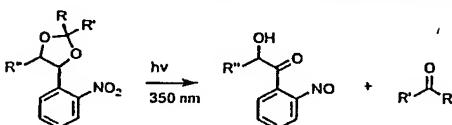
A. Linker for the formation of Ketones, Aldehydes, Amides and Acids



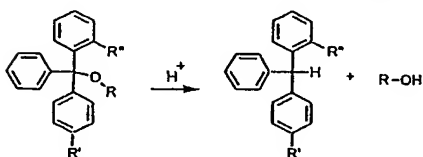
B. Linker for the formation of Ketones, Amides and Acids



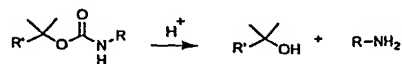
C. Linker for the formation of Aldehydes and Ketones



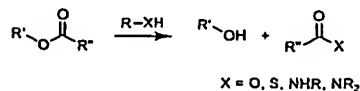
D. Linker for the formation of Alcohols and Acids



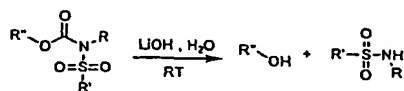
E. Linker for the formation of Amines and Alcohols



F. Linker for the formation of Esters, Thioesters, Amides, and Alcohols



G. Linker for the formation of Sulfonamides and Alcohols



X = O, HN, NR

X = O, S, NH, NR

2M K_3PO_4

$X = O, NHR', NR'_2$

TCEP = tris(2-carboxyethyl)phosphine

ROA

→

$$\xrightarrow{\text{H}_2\text{O} / \text{AgOH}}$$

AcOH

